Synthesis, characterization, magnetic properties, and topological aspects of isoskeletal heterometallic hexanuclear Co II 4 Ln III 2 coordination clusters possessing 2,3,4M6-1 Topology

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Synthesis, characterization, magnetic properties and topological aspects of isoskeletal heterometallic hexanuclear $Co^{II}_4Ln^{III}_2$ coordination clusters possessing 2,3,4M6-1 topology

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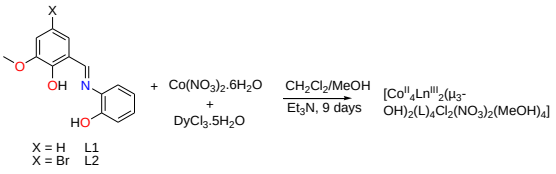
Abstract: The employment of (*E*)-2-(2-hydroxy-3-methoxybenzylideneamino)phenol (H_2L1) with $Co(NO_3)_2$ $6H_2O$ and $LnCl_3$ $x(H_2O)$ afforded a family of hexanuclear heterometallic coordination clusters (CCs) formulated $[Co^{II}_4Ln^{III}_2(\mu_3\text{-}OH)_2(L1)_4Cl_2(NO_3)_2(MeOH)_4]$ $3(Et_2O)$ where Ln is Y(**1**), Gd (**2**), Dy (**3**) and Tb (**4**). All the compounds are stable in solution as confirmed by ESI-MS studies. The topology of these compounds can be described as a twisted boat-like and enumerated as **2,3,4M6-1**. The use of (*E*)-2-(5-bromo-2-hydroxy-3-methoxybenzylideneamino)phenol (H_2L2) with $Co(NO_3)_2$ $6H_2O$ and $DyCl_3$ $x(H_2O)$ afforded an isoskeletal to **1** - **4** compound formulated as $[Co^{II}_4Dy^{III}_2(\mu_3\text{-}OH)_2(L2)_4Cl_2(NO_3)_2(MeOH)_4]$ (**5**). Magnetic studies performed in the temperature range 1.8 – 300K show that compound **3** shows a slow magnetic relaxation.

Introduction

Coordination clusters (CCs)[1] are of considerable modern interest in view of their aesthetically pleasant structures[2,3] relevance to nanoscience,[4,5] catalysis,[6–10] magnetic resonance[11] as well as applications in the area of molecule-based magnetic materials.[12–15] These molecules can be synthesized via self-assembly of organic or inorganic ligands with metal ions, following the hard soft base acid principle.[16] In this direction, depending on the nature of the organic ligand, that means the flexibility freedom as well the number of the available positions for coordination, ligand directed[17,18] or serendipitous[19,20] synthesis can be achieved. In the latter synthetic scheme, the structure of the cluster does not only depend upon the metal ions and the possible bridging modes for the ligands. Steric effects, template units, solvent, pH, concentration, counter anion can affect dramatically the shape of the final product. However, more efforts have been, now, focused on understanding the aforementioned factors as well to obtain access to molecules via a predictable manner.[21]

Lanthanide, especially Dy^{III}[22,23], and Co^{II}[24,25] based CCs have been widely used to gain access to molecules behaving as Single Molecule Magnets (SMMs). Interestingly, the combination of 3d and 4f ions has been proposed to be an efficient strategy to reach CCs with improved magnetic properties,[26] therefore the synthesis and magnetic properties of Co-Ln CCs has recently received tremendous attention and a plethora of Co-Ln CCs with variety of nuclearities $Co^{II}_2Ln^{III}$,[27,28] $Co^{II}_2Ln^{III}_2$,[29–33] $Co^{III}_2Ln^{III}_2$,[34,35] $Co^{II}Dy^{III}_3$,[33] $Co^{III}_2Dy^{III}_4$,[36,37] $Co^{II}_2Dy^{III}_4$,[38] $Co^{II}_3Dy^{III}_4$,[39] $Co^{II}_2Dy^{III}_5$,[33] $Co^{II}_4Ln^{III}_4$,[33,40] $Co^{II}_6Ln^{III}$,[41] $Co^{II}_2Co^{III}_4Ln^{III}_4$,[42] $Co^{II}_8Ln^{III}_2$,[43] $Co^{II}_2Dy^{III}_{10}$,[44] $Co^{II}_6Ln^{III}_8$,[43] $Co^{II}_8Ln^{III}_8$,[43,45] $Co^{II}_{11}Dy^{III}_6$,[40] $Co^{II}_9Co^{III}Ln^{III}_{42}$,[46] $Co^{II}_{16}Ln^{III}_{24}$,[47] have been reported.

On the other hand, (*E*)-2-(2-hydroxy-3-methoxybenzyli-deneamino)phenol (Scheme 1, left), initially reported in 1971 to capturing UO_2,[48] has recently received considerable attention in 3d and/or 4f chemistry, affording mainly low and high nuclearity CCs such as $Fe^{III}Ln^{III}_2$,[49,50] Zn^{II}_3,[51] Ni^{II}_4,[52] $Mn^{III}_2Ln^{III}_2$,[53] $Ni^{II}_2Ln^{III}_2$,[54] $Co^{II}_2Ln^{III}_2$,[32] Ln^{III}_4,[55] $Ni^{II}_4Ln^{III}_2$,[56] and $Ni^{III}_8Ln^{III}_4$.[57] Interestingly, the defect-dicubane $Co^{II}_2Dy^{III}_2$[32] shows SMM behavior with a blocking temperature of 22K (at 1500Hz).



Scheme 1. Synthetic conditions for the synthesis of $[Co^{II}_4Ln^{III}_2(\mu_3\text{-}OH)_2(L1)_4Cl_2(NO_3)_2(MeOH)_4]$ $3(Et_2O)$ clusters. Color code; Light blue-Gd^{III}; Pink-Co^{II}; Yellow-Carbon; Pale Blue-Nitrogen; Red-Oxygen; Green-Cl. Hydrogens omitted for clarity. (Right) The core of compound **1**.

With all these in mind, we decided to employ H_2L1 with $Co(NO_3)_2$ $6H_2O$ and $LnCl_3$ $x(H_2O)$ that resulted in a family of hexanuclear heterometallic CCs formulated as $[Co^{II}_4Ln^{III}_2(\mu_3\text{-}OH)_2(L1)_4Cl_2(NO_3)_2(MeOH)_4]$ $3(Et_2O)$ where Ln is Y (**1**), Gd (**2**), Dy (**3**) and Tb (**4**), in very good yields. For structural purposes, the employment of (*E*)-2-(5-bromo-2-hydroxy-3-methoxybenzylideneamino)phenol (H_2L2,[58] Scheme 1) under similar reaction conditions afforded an isoskeletal compound formulated as $[Co^{II}_4Dy^{III}_2(\mu_3\text{-}OH)_2(L2)_4Cl_2(NO_3)_2\text{-}(MeOH)_4]$ (**5**).

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Topological aspects and magnetic properties of these compounds are further discussed.

Results and Discussion

A combination of single crystal and powder X-Ray studies (Figure S1, see experimental section) show that compounds **1** - **4** are isoskeletal,[58] hence only the structure of **2** will be described. Three Et_2O molecules[59,60] could be successfully refined in the lattice of **2** and **3**. However, these samples are solvent sensitive and thus immediately lose their crystallinity. Powder XRD spectra of compounds **1** – **3** indicate phase purity.

Compound **2** crystallizes in the monoclinic space group $P2_1/c$. Four Co^{II} and two Gd^{III} cations form a twisted boat like core with, Co^{II} ions occupying the four central body positions and the two Gd^{III} ions occupying positions in the "bow" and "aft" (Figure 1), this will be assigned (1Ln : 4Co : 1Ln). The hexanuclear core is held together by two μ_3-OH groups between the Gd^{III} and the nearest two Co^{II} ions. Each of the four organic ligands adopts the same coordination mode (Figure S2) and is bonded to one Gd^{III} and two Co^{II} ions. Each ligand is chelated to a Co^{II} centre through one imino and two phenoxido oxygen atoms, forming a "metalloligand" which is further chelated to a Gd^{III} through a phenoxido and methoxido oxygen atom and another Co^{II} via the phenoxido oxygen atom of the aminophenol moiety. Each hydroxyl group bridges two Co^{II} and one Gd^{III} centres and the angles at are within the range 102.16(12)°-106.05(13)°. The coordination environment of Co2 and Co4 is fulfilled by a Cl atom. All Co centers adopt essentially distorted octahedral geometry, which the bond valence sum (BVS) analysis is indicative of oxidation state II (2.082, 1.900, 2.040 and 1.913 for Co1, Co2, Co3 and Co4, respectively).

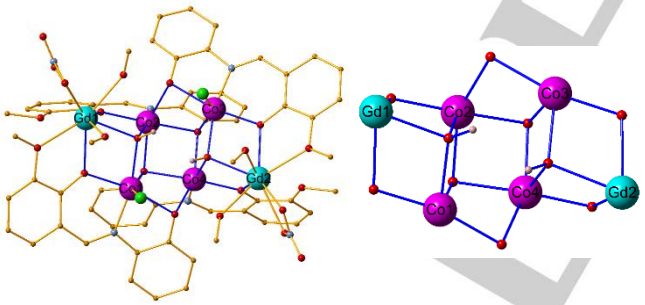


Figure 1. (Left) Molecular structure of compound **1**. Co1-Co4 shown in the body positions. Gd1 shown occupying the "bow" and Gd2 the "aft. Colour code; Light blue-Gd^{III}; Pink-Co^{II}; Yellow-Carbon; Pale Blue-Nitrogen; Red-Oxygen; Green-Cl. Hydrogens omitted for clarity. (Right) The core of compound **1**.

The coordination number of each Gd^{III} ion is 9. Using SHAPE software[61] the geometry of both Gd^{III} ions can be described as capped square antiprism with a S(P) agreement factor of 1.349. There are four $Gd^{III}\cdots Co^{II}$ distances within the range 3.4745(7) - 3.5837(7) Å and four $Co^{II}\cdots Co^{II}$ distances in the range 3.148 (7) -3.366(7) Å. The distance from the "bow" and "aft" between Gd^{III} ions is 7.680Å. There is no hydrogen bonding between adjacent entities, with spacing being well defined

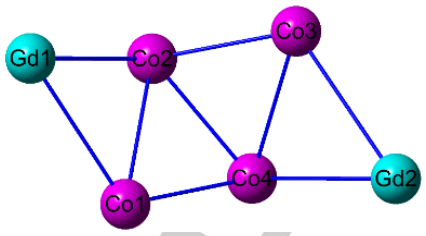
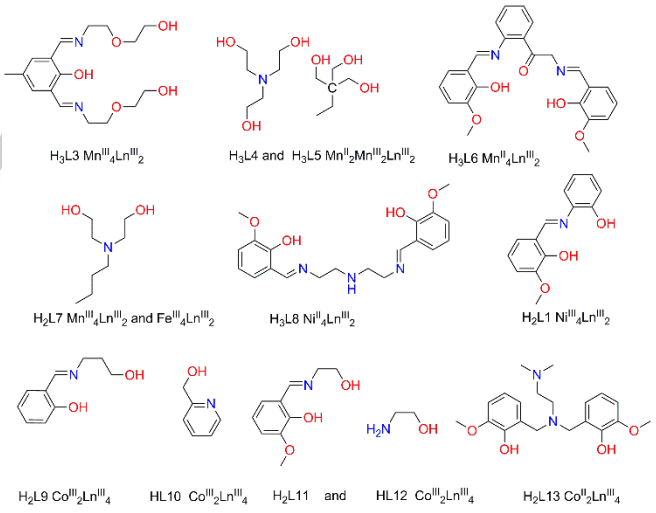


Figure 2. Representation of **2,3,4M6-1** decorated core of compound **1.**

To create an order in the expanding group of 3d/4f CCs, we have applied an algorithm which simplifies the topology of these species.[62] According to our nomenclature, the decorated core of these compounds can be enumerated as **2,3,4M6-1** (Figure 2). A literature survey indicates that the first example of this topology was found in a Co_2Na_4 compound.[63] The first 3d/4f CCs of this topology is a family of $Mn^{III}_4Ln_2$ (where Ln is Gd, Tb, Y) compounds build from ligand H_3L3 which were reported in 2008 by Oshi et al[64], in a ratio (2Mn : 2Ln :2Mn). Since then, few organic ligands, (Scheme 2) have been used for the synthesis of a several of 3d/Ln^{III} CCs with this topology. Ligands H_3L4, H_3L5 and H_3L6 gave access to $Mn^{II}_2Ln^{III}_4$ (1Mn : 4Ln : 1Mn)[53] and $Mn^{III}_2Mn^{II}_2Ln^{III}_2$ (1Ln : $1Mn^{III}$: $2Mn^{II}$: $1Mn^{III}$: 1Ln)[65]. In 2009, N-butyl-diethanolamine (H_2L7) was used to isolate a $Mn^{IV}_2Ce^{IV}_4$ (1Mn: 4Ce :1Mn)[66] CC, while recently its use resulted in the formation of the $Fe^{III}_4Dy^{III}_2$ (2Fe : 2Dy : 2Fe) CC.[67] Ligands H_3L8 and H_2L1 afforded $Ni^{II}_4Ln^{III}_2$ (1Ln : 4Ni : 1Ln)[56] and (2Ni : 2Dy : 2Ni)[68], respectively.



Scheme 2. The protonated form of the organic ligands used to for the synthesis of 3d/4f CCs possessing **2,3,4M6-1** topology.

More recently four series of Co/Ln^{III} CCs that possess the **2,3,4M6-1** topology have been described. The first example is a $Co^{III}_2Dy^{III}_4$ CC based on (E)-2-((3-hydroxypropylimino)methyl)phenol ligand (H_2L9, Scheme 2) showing slow magnetization relaxation.[36] The second example is a family of eight $Co^{III}_2Ln_4^{III}$ CCs (Ln is Sm, Pr, Eu, Gd, Tb, Dy, Ho, Er) constructed from ligand (HL10, Scheme 2). The Dy^{III} analogue exhibits slow relaxation of magnetization with a U_{eff} =

3.8k and t_o = 4.8 x 10^{-6}s.[37]. The third example is a series of four $Co^{II}_2Ln^{III}_4$ CCs constructed from ligands (H_2L11 and HL12, Scheme 2) (where Ln is Eu, Gd, Tb, Dy) reported by Du et al[69] in 2014, demonstrating the importance of Ln – O – Ln bond angles on magnetic coupling between to centers. The fourth example is a family of $Co^{II}_2Ln^{III}_4$ CCs (where Ln is Gd, Tb, Dy) derived from 6,6′-{(2-(dimethylamino)ethyl azanediyl)bis(methylene)}bis(2-methoxy-4-methylphenol) (H_2L13, Scheme 2), exhibiting slow magnetic relaxation behavior for the Dy analogue.[38] In all four reported families the Co/Ln ratio is 2/4 and all four Ln are close together, unlike the compounds reported in this work (**1** – **4**), the "bow" and "aft" positions are filled by Co^{II} cations (1Co : 4Ln : 1Co). To the best of our knowledge these are the first $Co^{II}_4Ln_2$ CCs that possess this topology.

It is worth nothing that despite H_2L11 offers similar coordination environment to H_2L1, its employment in Co/Ln chemistry lead to a hexanuclear CC with 2/4 Co/Ln ratio. This difference may be attributed to the *in situ* synthesis of ligand H_2L11.[69] Therefore, to further confirm the structural stability of the $Co^{II}_4Ln_2$ reported herein, we utilized the organic ligand H_2L2[58] (Scheme 1, right) under similar reaction conditions towards the synthesis of a Co/Dy CC. Ligand H_2L2 offers similar coordination environment to H_2L1. The reaction resulted in compound **5** (Figure 3) that can be considered to be isoskeletal to **1** – **4**.

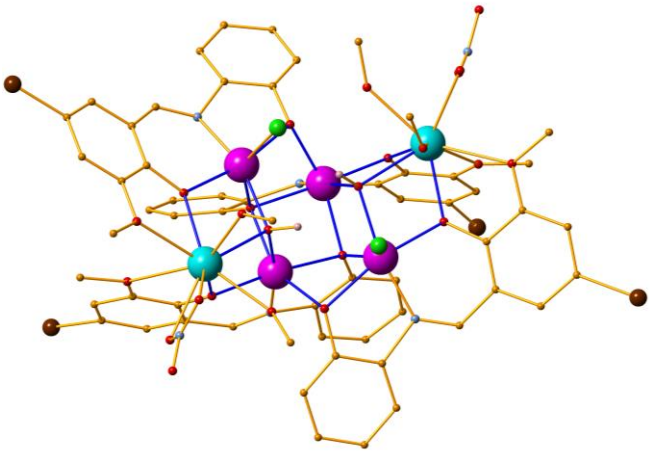


Figure 3. Molecular structure of compound **5**. Color code; Light blue-Dy^{III}; Pink-Co^{II}; Yellow-Carbon; Pale Blue-Nitrogen; Red-Oxygen; Green-Cl. Hydrogens omitted for clarity.

To confirm the identity of these compounds in solution, we made use of electrospray ionization mass spectrometry (ESI-MS). For **2**, we observed four peaks in the MS (positive-ion mode) at m/z 553.6409, 810.9421, 819.4479 and at m/z 828.8667 which correspond to the fragments, $[Co^{II}_4Ln^{III}_2(\mu_3\text{-}OH)_2(L1)_4(NO_3)_2(MeOH)_2]^{3+}$,$[Co^{II}_2Gd^{III}_2(\mu_3\text{-}OH)_2(L1)_4Cl_2+2H]^{2+}$, $[Co^{II}_2Gd^{III}_2(\mu_3\text{-}OH)_2(L1)_4Cl_2+2H+H_2O]^{2+}$ and $[Co^{II}_2Gd^{III}_2(\mu_3\text{-}OH)_2(L1)_4Cl_2+2H+2H_2O]^{2+}$, respectively (see Figures S3-6). A thermogravimetric (TGA) analysis of compounds **2** and **4** (Figure S7) showcases the solvent sensitivity (Et_2O and MeOH), whereas degradation begins at 300°C and 260°C, respectively. The final residue at 1000°C perfectly matches to a mixture of metal CoO/Gd_2O_3 (34.10% expected - 34.22% found) and CoO/Tb_4O_7 (33.31% expected - 33.22% found) oxides.

Variable-temperature direct-current (dc) magnetic susceptibility data were collected for compounds **1** - **4** in the temperature range 1.8–300 K in an applied field of 0.1 T. The data are shown as $\chi_M T$ vs. T plots in Figure 4. The χ_MT product of compound $Co^{II}_4Y^{III}_2$ (**1**) has a room temperature value of 11.13 $cm^3mol^{-1}K$ which is typical for four uncoupled Co^{II} ions, but larger than that for four free S=3/2 spins (χT=7.50cm^3.K.mol^{-1} and g=2.0) as a result of the presence of a significant spin orbital contribution in the susceptibility of octahedral high-spin Co^{II}.[24,25,70–73] Lowering the temperature the value of $\chi_M T$ gradual decreases and reaches a value of 2.17 cm^3Kmol^{-1} at 1.8K (Figure 4). In the case of CCs containing octahedral Co^{II} ion the decrease of the $\chi_M T$ at low temperature can be attributed to important spin orbital contribution and also dominant antiferromagnetic interaction between the four paramagnetic centers. The value of $\chi_M T$ at low temperature is low for four non coupling Co^{II} paramagnetic centers and suggests the presence of antiferomagnetic interaction between four paramagnetic centers. The latter observation is further by magnetization measurements at 2-5K. The magnetization does not saturate at the high-field limit (5T) of our instrument and the experimental value of the magnetization at 2.0K and 5T, is 6.12Nβ, which is low for four non coupled Co^{II} ions (Figure S8 in SI).[72]

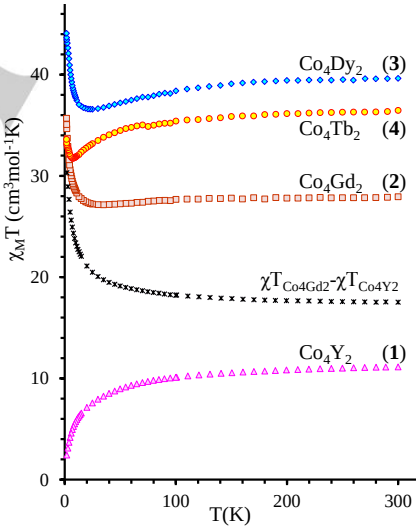


Figure 4. Temperature dependence of the χ_MT product at H_{dc}=0.1T for compounds **1** - **4**

The room temperature $\chi_M T$ value for **2** is 27.94 cm^3Kmol^{-1} which is slightly higher of the expected value for two non-interacting Gd^{III} (free ion; S = 7/2; g = 2)[73] and four Co^{II} centers as in compound **2**. The difference between the $\chi_M T$ value of **2** and **1** at 300K is 17.51 cm^3Kmol^{-1} which is higher of the theoretical expected for two Gd^{III} ions (15.75 cm^3Kmol^{-1}). This can be justified by the presence of ferromagnetic interaction (in conjunction with antiferromagnetic coupling in Co_4 core) as well the small variation of g factor for octahedral Co^{II}. By decreasing the temperature the $\chi_M T$ product decreases steadily up to a value of 27.15 $cm^3mol^{-1}K$ at 30 K. Upon lowering to 30K, a rapid increase of the $\chi_M T$ value is observed indicating the presence of ferromagnetic interaction in **2**. The temperature dependence of

difference between $\chi_M T$ value of **2** and $\chi_M T$ value of **1** (see black stars in Figure 4) suggest that the ferromagnetic interaction is operated between the Gd ions and Co_4 core. The field dependence of magnetization of compound **2** confirms the presence of important (non zero) spin state with significant component of anisotropy.

The room temperature $\chi_M T$ values for **3** (Co_4Dy_2) and **4** (Co_4Tb_2) (39.62 and 36.46 cm^3Kmol^{-1}, respectively) are slightly higher of the expected values for two non-interacting Dy^{III} ($^6H_{15/2}$ free ion; S = 5/2; L = 5; J=15/2; g_J = 4/3), Tb($^7F_6$ free ion; S = 3; L = 3; J=6; g_J = 3/2) and four Co^{II} centers.[74,75] Similar to Gd analogue the temperature dependence of $\chi_M T$ values has a minimum at 25 and 7K for **3** and **4**, respectively. Upon further temperature decrease, the $\chi_M T$ product increase to reach the values of 44.07 and 33.61 cm^3Kmol^{-1} for **3** and **4**, respectively. This behavior suggests the presence of same ferromagnetic interaction between Co_4 core and lanthanides ions in **3** and **4**.

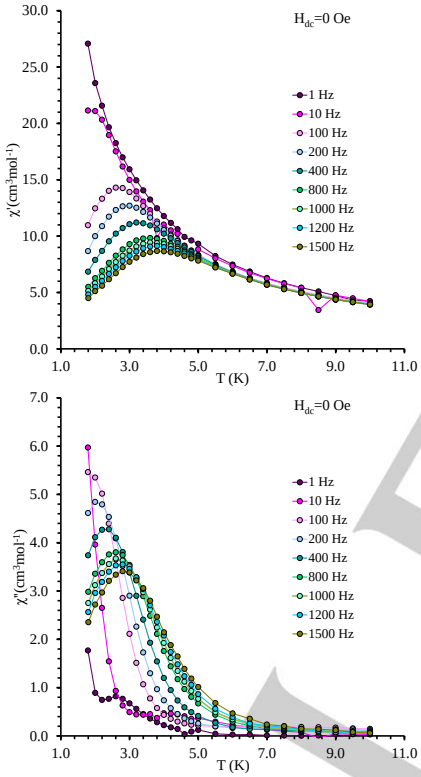


Figure 5. Temperature dependence of the in-phase (χ') and out-of-phase (χ") *ac* susceptibility for **3** at indicated frequencies at zero applied *dc* field.

The dynamic properties of **1** - **4** compounds have been investigated using *ac* susceptibility measurements as a function of temperature at different frequency and also at different temperature as function of frequency at 4.0Oe oscillating field between 1 and 1500Hz. Compounds **1**, **2** and **4** do not show out-of-phase signal at zero *dc* magnetic field. No modifications in out-of-phase susceptibility after applying the *dc* magnetic field (0-3.0T) are detected for **1**, **2** and **4**. In the case of compound **3** at H_{dc}=0 the magnetic field ac measurement clearly shows presence of out-of-phase signal χ'' in *ac* susceptibility with strong temperature and frequency dependence (Figure 5). The effective barrier of slow magnetic relaxation U_{eff} is obtained according the Arrhenius law from temperature (Figure S10) measurements (U_{eff}(**3**)=13.4K τ_o=8.5×10^{-7})

The *ac* susceptibility follow the generalized Debye model[76,77] Simultaneous fitting of $\chi'(\nu)$, $\chi''(\nu)$ and Cole-Cole plot are shown in Figure S11. The relatively large value of α (0.015-0.388) indicates that more than one relaxation process generated by QTM might be operational at this condition.

Conclusions

Our synthetic strategy to utilize the dianionic ligand H_2L1 (Scheme 1, right) in Co/Ln chemistry, resulted in a family of hexametallic $Co^{II}_4Ln_2$ (**1** – **4**) CCs possessing a **2,3,4M6-1** topology. To the best of our knowledge, compounds **1** – **4** are the first $Co^{II}_4Ln_2$ examples of this topology. The use of H_2L2 (Scheme 1, right), which provides coordination modes similar to those of H_2L1, in a similar synthetic strategy that afforded **1** – **4**, results in the formation of compound **5** that is isoskeletal to **1** – **4**. However when H_2L10, which provides coordination modes similar to those of H_2L1, was employed in Co/Ln chemistry afforded a **2,3,4M6-1** topology but with different formula. Our future studies will be focused in two different directions: a) to perform a systematic synthetic study by employing more organic ligands, which offer similar coordination environments to H_2L1, H_2L2 and H_2L10, in Co/Ln chemistry to afford hexanuclear CCs bearing **2,3,4M6-1** topology and b) to further develop our topological approach[78] by including valuable information for the synthesis of a specific topology. Finally, magnetic studies of **1** – **4**, show the presence of ferro- and antiferromagnetic interactions and interestingly, compound **3** shows SMM behavior.

Experimental Section

Materials and Methods. All the $LnCl_3$ xH_2O salts were prepared by reaction of lanthanide oxide with corresponding acid in hot aqueous solution and crystallized by slow evaporation. The commercially available $Co(NO_3)_2$ $6H_2O$, Et_3N, MeOH and Et_2O were used as received without further purification. Fourier Transform IR spectra were measured on a Perkin-Elmer Spectrum One spectrometer with samples prepared as KBr pellets. X-ray powder diffraction patterns were recorded using a Bruker-AXS D8-Advance diffractometer equipped with a Cu sealed-tube radiation source (λ = 1.5418 Å) and a secondary beam graphite monochromator. Data were collected from 4° to 50° in the 2θ mode at 5 s/step at the University of Ioannina. TGA analysis was performed on a TA Instruments Q-50 model (TA, Surrey, UK) under nitrogen and at a scan rate of 10 °C/min.

Synthetic part. Ligands H_2L1 and H_2L2 were synthesized according to the literature.[58] Compounds **1-4** were synthesized using the same method, therefore only the synthesis of **1** is described here. H_2L_1 (48mg, 0.2mmol) was suspended in a mixture of CH_2Cl_2 (10mL) and MeOH (5mL) and stirred for 5 minutes before the addition of $Co(NO_3)_2.6H_2O$ (58mg, 0.2mmol), $GdCl_3.xH_2O$ (37mg,0.1mmol) and Et_3N (0.42mmol, 59.2μL). The resultant solution was stirred for 2h, upon which time it was filtered and the filtrate underwent vapor diffusion with Et_2O. After 9 days small red crystals were collected with a yield of 68% based on Gd. IR (ν, cm^{-1}) = 3293, 1782, 1609, 1552, 1454, 1388, 1291, 1224, 1182, 1073, 1033, 964, 820, 733, 635. A similar procedure was followed for the synthesis of compound **5**, using H_2L2 instead of H_2L1. IR (ν, cm^{-1})= 3290, 1605, 1551, 1452, 1389, 1295, 1228, 1183, 1076, 1035, 965, 819, 735, 638.

Magnetic studies. Magnetic susceptibility measurements were carried out on polycrystalline samples with a MPMS5 Quantum Design

susceptometer working in the range 30–300 K under an external magnetic field of 0.3 T and under a field of 0.03 T in the 30–2 K range to avoid saturation effects. Diamagnetic corrections were estimated from Pascal Tables.

Crystallography. Data for **2**, **4** and **5** were collected (ω-scans) at the University of Sussex using an Agilent Xcalibur Eos Gemini Ultra diffractometer with a CCD plate detector under a flow of nitrogen gas at 173(2) K using Mo Kα radiation (λ = 0.71073 Å). CRYSALIS CCD and RED software were used respectively for data collection and processing. Reflection intensities were corrected for absorption by the multi-scan method. All structures were determined using Olex2[79], solved using either Superflip[80] or SHELXT[81,82] and refined with SHELXL-2014.[83] All non-H atoms were refined with anisotropic thermal parameters, and H-atoms were introduced at calculated positions and allowed to ride on their carrier atoms. Crystal data and structure refinement parameters for all compounds are given in Tables S1 and S2. Geometric/crystallographic calculations were performed using Olex2[79] package; graphics were prepared with Crystal Maker. $C_{132}H_{154}Cl_4Co_8Gd_4N_{12}O_{51}$ (2): M =3966.90 g/mol, monoclinic, space group $P2_1/c$ (no. 14), a = 15.7924(10) Å, b = 21.4805(10) Å, c = 25.0254(15) Å, β = 98.932(5)°, V = 8386.4(8) Å^3, Z = 2, T = 173.0 K, μ(MoKα) = 2.468 mm^{-1}, $Dcalc$ = 1.571 g/cm^3, 40735 reflections measured (4.134° ≤ 2Θ ≤ 50.216°), 14671 unique (R_{int} = 0.0489, R_{sigma} = 0.0566) which were used in all calculations. The final R_1 was 0.0386 (I > 2σ(I)) and wR_2 was 0.0944 (all data). $C_{132}H_{152}Cl_4Co_8N_{12}O_{51}Tb_4$ (4) : M =3971.57 g/mol, monoclinic, space group $P2_1/c$ (no. 14), a = 15.7073(6) Å, b = 21.4916(12) Å, c = 24.8869(10) Å, β = 98.906(3)°, V = 8299.9(7) Å^3, Z = 2, T = 173 K, μ(MoKα) = 2.600 mm^{-1}, $Dcalc$ = 1.589 g/cm^3, 51014 reflections measured (4.136° ≤ 2Θ ≤ 51.424°), 15501 unique (R_{int} = 0.0805, R_{sigma} = 0.0652) which were used in all calculations. The final R_1 was 0.0386 (I > 2σ(I)) and wR_2 was 0.0956 (all data). $C_{60}H_{58}Br_4Cl_2Co_4Dy_2N_6O_{24}$ (**5**): M =2198.38 g/mol, trigonal, space group $P3_121$ (no. 152), a = 16.2445(5) Å, c = 29.8880(11) Å, V = 6830.3(5) Å^3, Z = 3, T = 173.0 K, μ(MoKα) = 4.209 mm^{-1}, $Dcalc$ = 1.603 g/cm^3, 16320 reflections measured (5.198° ≤ 2Θ ≤ 49.528°), 6612 unique (R_{int} = 0.0844, R_{sigma} = 0.1090) which were used in all calculations. The final R_1 was 0.0452 (I > 2σ(I)) and wR_2 was 0.0965 (all data). CCDC-1450563 (**2**), CCDC-1450564 (**4**), CCDC-1450565 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Keywords: coordination clusters • cobalt • lanthanide • magnetic properties • topology

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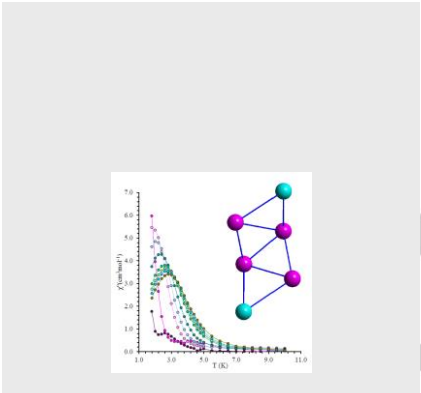
Entry for the Table of Contents (Please choose one layout)

Layout 1:

FULL PAPER

Text for Table of Contents

The use of a diprotic Schiff base ligand (H_2L1) with $Co(NO_3)_2$ $6H_2O$ and $LnCl_3$ $x(H_2O)$ afforded a family of hexanuclear coordination clusters formulated as $[Co^{II}_4Ln^{III}_2(\mu_3\text{-}OH)_2(L1)_4Cl_2(NO_3)_2(MeOH)_4]$ $3(Et_2O)$ where Ln is Y(**1**), Gd (**2**), Dy (**3**) and Tb (**4**). The topology of these compounds can be enumerated as **2,3,4M6-1**. Compound 3 shows Single Molecule Magnet (SMM) behavior.
*Single Molecule Magnets



Co^{II}-Dy^{III} Single Molecule Magnets

Kieran Griffiths, Ghenadie Novitchi[] and George E. Kostakis,**

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Synthesis, characterization, magnetic properties and topological aspects of isoskeletal heterometallic hexanuclear $Co^{II}_4Ln^{III}_2$ coordination clusters possessing 2,3,4M6-1 topology